

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 : <b>C11D 17/00, 3/37</b>		A1	(11) International Publication Number: <b>WO 91/08281</b>
			(43) International Publication Date: <b>13 June 1991 (13.06.91)</b>
(21) International Application Number: <b>PCT/EP90/01815</b>		(74) Agent: JOPPE, Hermina, L., P.; Unilever N.V., Patent Division, P.O. Box 137, NL-3130 AC Vlaardingen (NL).	
(22) International Filing Date: <b>24 October 1990 (24.10.90)</b>		(81) Designated States: AU, BR, CA, CH (European patent), DE (European patent), ES (European patent), FR (European patent), GB (European patent), IT (European patent), JP, NL (European patent), SE (European patent), US.	
(30) Priority data: <b>8927361.9 4 December 1989 (04.12.89) GB</b>		Published With international search report.	
(71) Applicant (for AU CA GB only): UNILEVER PLC [GB/GB]; Unilever House, Blackfriars, London EC4P 4BQ (GB).		<p>PAA - PED</p> <p>comb-type polymer</p>	
(71) Applicant (for all designated States except AU CA GB US): UNILEVER N.V. [NL/NL]; P.O. Box 137, NL-3000 DK Rotterdam (NL).			
(72) Inventors; and (75) Inventors/Applicants (for US only) : FOSTER, Francis, Geoffrey [GB/GB]; 4 Westway, Greasby, Wirral Merseyside (GB). VAN DE PAS, Johannes, Cornelis [NL/NL]; Philips Willemstraat 6, NL-3136 CV Vlaardingen (NL).			
(54) Title: LIQUID DETERGENTS			
(57) Abstract			
<p>A liquid detergent composition comprising a dispersion of lamellar droplets of detergent active materials in an aqueous continuous phase and one or more ingredients for providing softness to fabrics, said composition also comprising a deflocculating polymer.</p> <p><i>deflocculating polymer. comb-type, comb-like</i></p> <p><i>polymer combs</i></p> <p><i>polyester (no sulfonic acid group)</i></p> <p><i>OR</i></p> <p><i>sulfonate salt + ester linkage (no polyester)</i></p> <p><i>page 4-8</i></p> <p><i>Side chain:</i></p>			

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	FI	Finland	ML	Mali
AU	Australia	FR	France	MN	Mongolia
BB	Barbados	GA	Gabon	MR	Mauritania
BE	Belgium	GB	United Kingdom	MW	Malawi
BF	Burkina Faso	GN	Guinea	NL	Netherlands
BG	Bulgaria	GR	Greece	NO	Norway
BJ	Benin	HU	Hungary	PL	Poland
BR	Brazil	IT	Italy	RO	Romania
CA	Canada	JP	Japan	SD	Sudan
CF	Central African Republic	KP	Democratic People's Republic of Korea	SE	Sweden
CG	Congo	KR	Republic of Korea	SN	Senegal
CH	Switzerland	LJ	Liechtenstein	SU	Soviet Union
CI	Côte d'Ivoire	LK	Sri Lanka	TD	Chad
CM	Cameroon	LU	Luxembourg	TG	Togo
DE	Germany	MC	Monaco	US	United States of America
DK	Denmark	MG	Madagascar		
ES	Spain				

LIQUID DETERGENTS

The present invention is concerned with aqueous liquid detergent compositions which contain sufficient detergent-active material and, optionally, sufficiently dissolved electrolyte to result in a structure of lamellar droplets dispersed in a continuous aqueous phase. In particular the present invention relates to liquid detergent compositions for washing of fabrics and providing said fabrics with a softening benefit.

Lamellar droplets are a particular class of surfactant structures which, inter alia, are already known from a variety of references, e.g. H.A.Barnes, 'Detergents', Ch.2. in K.Walters (Ed), 'Rheometry: Industrial Applications', J. Wiley & Sons, Letchworth 1980.

Such lamellar dispersions are used to endow properties such as consumer-preferred flow behaviour and/or turbid appearance. Many are also capable of suspending particulate solids such as detergency builders or abrasive particles. Examples of such structured liquids without suspended solids are given in US patent 4 244 840, whilst examples where solid particles are suspended are disclosed in specifications EP-A-160 342; EP-A-38 101; EP-A-104 452 and also in the aforementioned US 4 244 840. Others are disclosed in European Patent Specification EP-A-151 884, where the lamellar droplet are called 'spherulites'.

The presence of lamellar droplets in a liquid detergent product may be detected by means known to those skilled in the art, for example optical techniques, various rheometrical measurements. X-ray or neutron diffraction, and electron microscopy.

The droplets consist of an onion-like configuration of concentric bi-layers of surfactant molecules, between

which is trapped water or electrolyte solution (aqueous phase). Systems in which such droplets are close-packed provide a very desirable combination of physical stability and solid-suspending properties with useful  
5 flow properties.

The viscosity and stability of the product depend on the volume fraction of the liquid which is occupied by the droplets. Generally speaking, when the volume  
10 fraction is around 0.6, the droplets are just touching (space-filling). This allows reasonable stability with an acceptable viscosity (say no more than 2.5 Pas, preferably no more than 1 Pas at a shear rate of  $21\text{s}^{-1}$ ). This volume fraction also endows useful solid-  
15 suspending properties.

A problem in the formulating of liquid detergent compositions is to prevent the occurrence of flocculation. When flocculation occurs between the  
20 lamellar droplets at a given volume fraction, the viscosity of the corresponding product will increase due to the formation of a network throughout the liquid. Flocculation may also lead to instability reflected in phase separation of the product.

25 A problem in the formulation of liquid detergent compositions which are capable of providing a softening benefit to fabrics is that the addition of softening ingredients often causes instability and/or  
30 unacceptable high viscosity of the product.

It has now been found, that liquid detergent compositions having improved stability and/or viscosity properties can be obtained by incorporating therein a  
35 deflocculating polymer.

Accordingly the present invention relates to a liquid detergent composition comprising a dispersion of

lamellar droplets of detergent active materials in an aqueous continuous phase and one or more ingredients for providing softness to fabrics, said composition also comprising a deflocculating polymer.

5

The deflocculating polymer

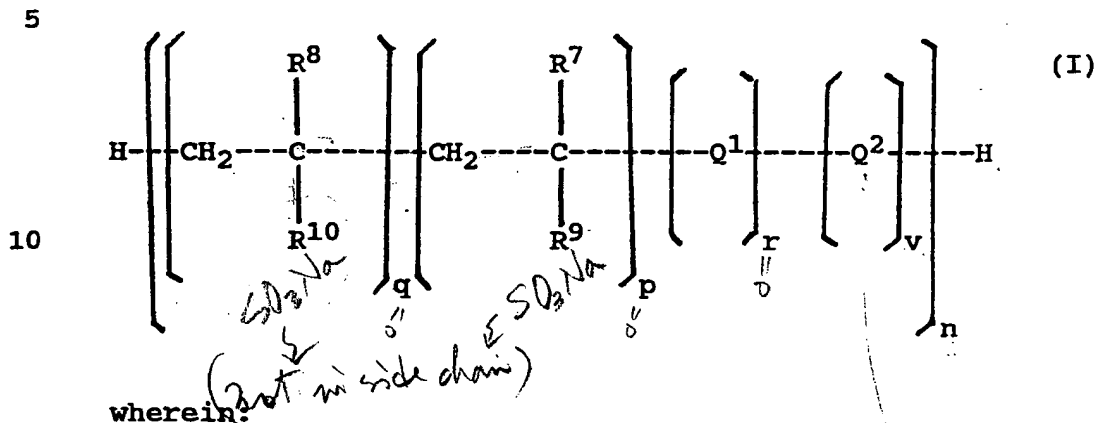
Suitable deflocculating polymers for use in compositions of the present invention are for instance described in our co-pending European patent application 10 89201530.6 (EP 346 995). Polymers as described in this patent have a hydrophilic backbone and at least one hydrophobic side chain.

Generally the hydrophilic backbone of the polymer is 15 predominantly linear (the main chain of the backbone constitutes at least 50 %, preferably more than 75 %, most preferred more than 90% by weight of the backbone), suitable monomer constituents of the hydrophilic backbone are for example unsaturated C<sub>1-6</sub> 20 acids, ethers, alcohols, aldehydes, ketones or esters, sugar units, alkoxy units, maleic anhydride and saturated polyalcohols such as glycerol. Examples of suitable monomer units are acrylic acid, methacrylic acid, maleic acid, vinyl acetic acid, glucosides, 25 ethylene oxide and glycerol. The hydrophilic backbone made from the backbone constituents in the absence of hydrophobic side-groups is relatively water-soluble at ambient temperature and a pH of between 6.5 and 14.0. Preferably the solubility is more than 1 g/l, more 30 preferred more than 5 g/l most preferred more than 10 g/l.

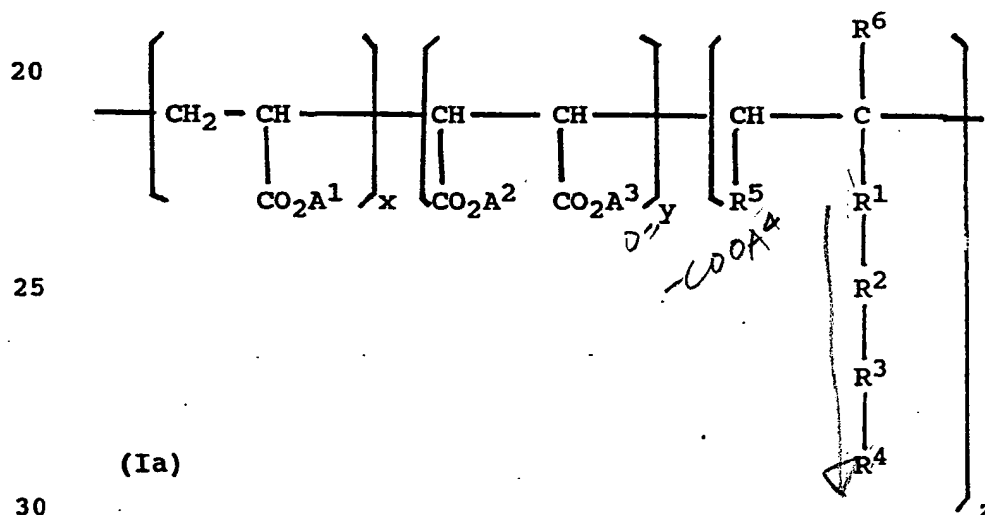
Preferably the hydrophobic sidegroups are composed of 35 relatively hydrophobic alkoxy groups for example butylene oxide and/or propylene oxide and/or alkyl or alkenyl chains having from 5 to 24 carbon atoms. The hydrophobic groups may be connected to the hydrophilic

backbone via relatively hydrophilic bonds for example a poly ethoxy linkage.

Preferred polymers are of the formula:



15  $\text{Q}^2$  is a molecular entity of formula (Ia):



wherein:

35  $\text{R}^1$  represents  $-\text{CO}-\text{O}-$ ,  $-\text{O}-$ ,  $-\text{O}-\text{CO}-$ ,  $-\text{CH}_2-$ ,  $-\text{CO}-\text{NH}-$  or is absent;

$\text{R}^2$  represents from 1 to 50 independently selected alkyleneoxy groups preferably ethylene oxide or

propylene oxide groups, or is absent, provided that when  $R^3$  is absent and  $R^4$  represents hydrogen or contains no more than 4 carbon atoms, then  $R^2$  must contain an alkyleneoxy group preferably more than 5  
5 alkyleneoxy groups with at least 3 carbon atoms;

$R^3$  represents a phenylene linkage, or is absent;

10  $R^4$  represents hydrogen or a  $C_{1-24}$  alkyl or  $C_{2-24}$  alkenyl group, with the provisos that

- a) when  $R^1$  represents  $-O-CO-$ ,  $R^2$  and  $R^3$  must be absent and  $R^4$  must contain at least 5 carbon atoms;  
b) when  $R^2$  is absent,  $R^4$  is not hydrogen and when also  
15  $R^3$  is absent, then  $R^4$  must contain at least 5 carbon atoms;

$R^5$  represents hydrogen or a group of formula  $-COOA^4$ ;

20  $R^6$  represents hydrogen or  $C_{1-4}$  alkyl; and

$A^1$ ,  $A^2$ ,  $A^3$  and  $A^4$  are independently selected from hydrogen, alkali metals, alkaline earth metals, ammonium and amine bases and  $C_{1-4}$ , or  $(C_2H_4O)_tH$  wherein  
25  $t$  is from 1-50, and wherein the monomer units may be in random order.

$Q^1$  is a multifunctional monomer, allowing the branching of the polymer, wherein the monomers of the polymer may be connected to  $Q^1$  in any direction, in any order,  
30 therewith possibly resulting in a branched polymer. Preferably  $Q^1$  is trimethyl propane triacrylate (TMPTA), methylene bisacrylamide or divinyl glycol.

$z$  and  $v$  are 1;  $n$  is at least 1;  $(x + y + p + q + r) : z$   
35 is from 4 : 1 to 1,000 : 1, preferably from 6 : 1 to 250 : 1; in which the monomer units may be in random order; and preferably  $p$  and  $q$  are zero and/or  $r$  is zero; most preferably  $p$ ,  $q$ ,  $y$  and  $r$  are zero.

R<sup>7</sup> and R<sup>8</sup> represent -CH<sub>3</sub> or -H;

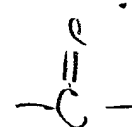
R<sup>9</sup> and R<sup>10</sup> represent substituent groups such as amino,  
 5 amine, amide, sulphonate, sulphate, phosphonate,  
 phosphate, hydroxy, carboxyl and oxide groups,  
 preferably they are selected from  $\text{-SO}_3\text{Na}$ ,  $\text{-CO-O-C}_2\text{H}_4\text{-}$ ,  
 $\text{OSO}_3\text{Na}$ ,  $\text{-CO-O-NH-C(CH}_3)_2\text{-SO}_3\text{Na}$ ,  $\text{-CO-NH}_2$ ,  $\text{-O-CO-CH}_3$ , -  
 OH;

10 Preferably polymers for use in compositions of the  
 invention which are of relatively high pH (say 10 or  
 more) are substantially free of hydrolysable groups  
 such as carbonyl groups for increased polymer stability  
 at high pH values. Particularly preferred polymers for  
 15 use in high pH compositions of the invention comprise  
 hydrophilic backbones constituted by acid groups such  
 as acrylic acid and at least one hydrophobic side chain  
 which is constituted of from 5 to 75 relatively water-  
 insoluble alkoxy groups such as propoxy units  
 20 optionally linked to the hydrophylic backbone via an  
 poly-alkoxy linkage constituted of from 1-10 relatively  
 watersoluble alkoxy groups such as ethoxy units.

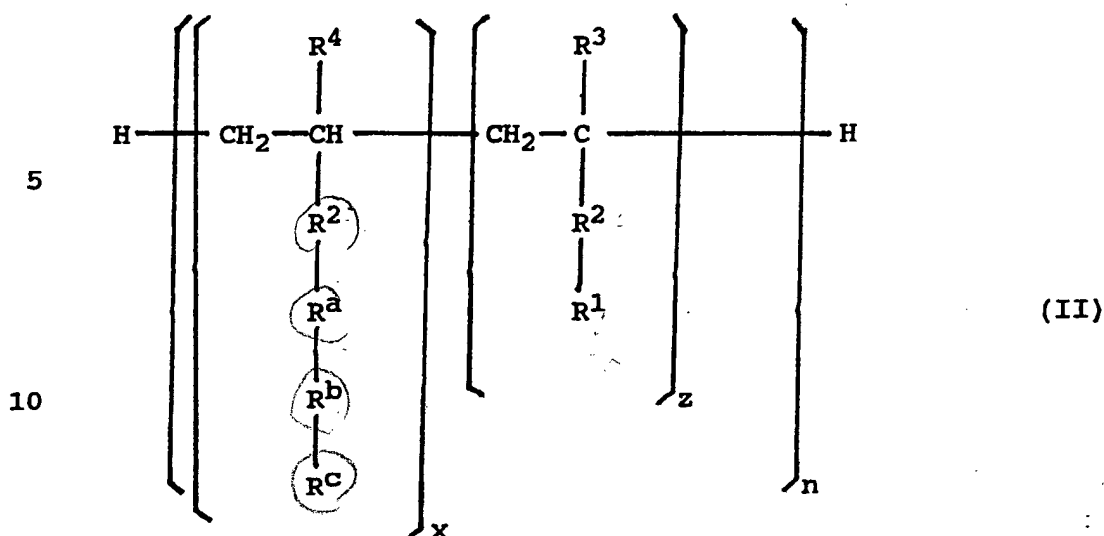
Other preferred polymers for use in compositions of the  
 25 invention are described in our co-pending British patent  
 applications 8924479.2, 8924478.4 and 8924477.6. Of the  
 polymers described in those patent applications,  
 especially the use of polymers in accordance with

GB patent application 8924478.4 is preferred. These  
 30 polymers are constituted of nonionic monomers and ionic  
 monomers, wherein the ionic monomer is from 0.1 to 50 %  
 by weight of the polymer. Especially preferred polymers  
 of this type are of the formula:

35

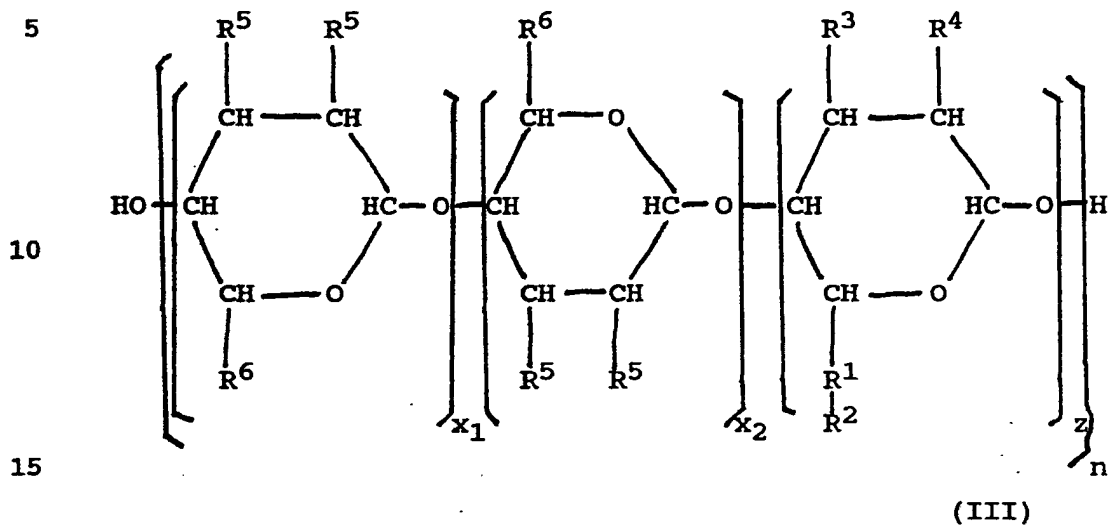






- 15 wherein: x, z and n are as above;
- R<sup>3</sup> and R<sup>4</sup> represent hydrogen or C<sub>1-4</sub> alkyl;
  - R<sup>2</sup> represents -CO-O-, -O-, -O-CO-,  
-CH<sub>2</sub>-, -CO-NH-, or is absent;
  - R<sup>1</sup> represents -C<sub>3</sub>H<sub>6</sub>-N<sup>+</sup>-(CH<sub>3</sub>)<sub>3</sub>(Cl<sup>-</sup>),  
20 -C<sub>2</sub>H<sub>4</sub>-OSO<sub>3</sub><sup>-</sup>(Na<sup>+</sup>), -SO<sub>3</sub><sup>-</sup>(Na<sup>+</sup>),  
-C<sub>2</sub>H<sub>4</sub> N<sup>+</sup>(CH<sub>3</sub>)<sub>3</sub> Cl<sup>-</sup>, -C<sub>2</sub>H<sub>4</sub> N<sup>+</sup> (C<sub>2</sub>H<sub>6</sub>)<sub>3</sub> Cl<sup>-</sup>,  
-CH<sub>2</sub> N<sup>+</sup> (CH<sub>3</sub>)<sub>3</sub> Cl<sup>-</sup>, -CH<sub>2</sub> N<sup>+</sup> (C<sub>2</sub>H<sub>6</sub>)<sub>3</sub> Cl<sup>-</sup> or  
benzyl-SO<sub>3</sub><sup>-</sup>(Na<sup>+</sup>);
  - R<sup>a</sup> is CH<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>3</sub>H<sub>6</sub> or is absent;
  - 25 - R<sup>b</sup> represents from 1 to 50 independently  
selected alkylene oxide groups, preferably  
ethylene oxide groups or is absent;
  - R<sup>c</sup> represents -OH or -H;
- 30 and wherein if R<sup>2</sup>, R<sup>a</sup> and R<sup>b</sup> are absent, then R<sup>c</sup> is  
not -H.

Other preferred polymers have the formula:



Wherein:

- $x = x_1 + x_2$
- 20 -  $x, z$  and  $n$  are as defined above
- $R^1$  represents  $-\text{CH}_2\text{O}-$  or  $-\text{O}-$ ;
- $R^2$  represents  $-\text{CH}_2\text{COO}^-\text{Na}^+$ ,  $-\text{C}_3\text{H}_6\text{ON}^+(\text{CH}_3)_3\text{Cl}^-$  or  $-\text{C}_3\text{H}_3\text{N}^+(\text{CH}_3)_3\text{Cl}^-$
- $R^3$  and  $R^4$  represents  $-\text{OH}$ ,  $\text{CH}_2\text{OH}$ ,  $-\text{O}(\text{C}_3\text{H}_6\text{O})_p\text{-H}$ ,
- 25  $-\text{CH}_2-\text{O}(\text{C}_3\text{H}_6\text{O})_p\text{-H}$  or  $-\text{OCH}_2\text{COO}^-\text{Na}^+$  or  $-\text{O}-\text{C}_3\text{H}_6\text{ON}^+(\text{CH}_3)_3\text{Cl}^-$  or  $-\text{O}-\text{C}_3\text{H}_6\text{N}^+(\text{CH}_3)_3\text{Cl}^-$
- $R^5$  represents  $-\text{OH}$ ,  $-\text{NH}-\text{CO}-\text{CH}_3$  or  $-\text{O}(\text{C}_3\text{H}_6\text{O})_p\text{-H}$
- $R^6$  represents  $-\text{OH}$ ,  $-\text{CH}_2\text{OH}$ ,  $-\text{CH}_2-\text{OCH}_3$ ,  $-\text{O}(\text{C}_3\text{H}_6\text{O})_p\text{-H}$  or  $-\text{CH}_2-\text{O}-(\text{C}_3\text{H}_6\text{O})_p\text{-H}$
- 30 -  $p$  is from 1 - 10.

Preferably polymers for use in compositions have a molecular weight (as determined as in our co-pending european patent application 89201530.6) of between 500 and 100,000, more preferred from 1,000 to 20,000, especially preferred from 1,500 to 10,000 most preferred from 2,800 to 6,000. Polymers for use in compositions of the invention may for example be prepared by using

conventional aqueous polymerisation procedures, suitable methods are for example described in the above mentioned co-pending european patent application.

- 5 Generally the deflocculating polymer will be used at from 0.01 to 5 % by weight of the composition, more preferably from 0.1 to 3.0, especially preferred from 0.25 to 2.0 %.
- 10 Without being bound by any particular interpretation or theory, the Applicants have hypothesised that the polymers exert their action on the composition by the following mechanism. The hydrophobic side-chain(s) or ionic groups could be incorporated in or onto the outer
- 15 bi-layer of the droplets, leaving the hydrophilic or nonionic backbone over the outside of the droplets and/or the polymers could be incorporated deeper inside the droplet.
- 20 When the hydrophobic or side chains or ionic groups are mainly incorporated in or onto the outer bilayer of the droplets, this has the effect of decoupling the inter- and intra-droplet forces i.e. the difference between the forces between individual surfactant molecules in
- 25 adjacent layers within a particular droplet and those between surfactant molecules in adjacent droplets could become accentuated in that the forces between adjacent droplets are reduced. This will generally result in an increased stability due to less flocculation and a
- 30 decrease in viscosity due to smaller forces between the droplets resulting in greater distances between adjacent droplets.
- 35 When the polymers are incorporated deeper inside the droplets also less flocculation will occur, resulting in an increase in stability. The influence of these polymers within the droplets on the viscosity is governed by two opposite effects : firstly the presence

of deflocculating polymers will decrease the forces between adjacent droplets resulting in greater distances between the droplets, generally resulting in a lower viscosity of the system; secondly the forces between the layers within the droplets are equally reduced by the presence of the polymers in the droplet, this generally result in an increase in the layer thickness, therewith increasing the lamellar volume of the droplets, therewith increasing the viscosity. The net effect of these two opposite effects may result in either a decrease or an increase in the viscosity of the product.

Preferred compositions according to the invention are stable and have a relatively low viscosity. Preferably a corresponding composition minus the deflocculating polymer is less stable and/or has a higher viscosity.

#### The fabric softening ingredients

There has been a desire to provide single liquid detergent compositions which would be capable of both washing and softening the fabrics to overcome the inconvenience of using separate products for in-the-rinse softening.

British patent application GB 1,400,898 (Procter and Gamble) describes the use of smectic-type clays in granular detergent compositions for obtaining softening in the wash. Hitherto, however, it has been difficult to incorporate clay softeners in liquid aqueous detergent compositions.

EP 225 142 (UNILEVER) proposes to solve the instability and/or the viscosity problems, by using a fabric softening clay material having a limited swellability.

EP 291 261 (UNILEVER) proposes to solve the instability and/or the viscosity problems, by using a fabric

softening clay material in combination with non-peptising/non-building electrolytes such as sodium formate, chloride or sulphate.

5 EP 213 730 (UNILEVER) proposes to provide the desired softening in the wash, by combining a detergent active material, a fabric softening agent and specific low gel-point cellulose ether derivatives. These specific cellulose ethers are capable of enhancing fabric  
10 softening in the wash step.

EP 265 187 discloses the use of imidazoline particles having an average particle diameter of from about 20 to 200 microns for softening-in-the wash.

15 EP 294 893 discloses the use of imidazoline-anionic surfactant ion-pair/wax composites as fiber- and fabric conditioning agent. EP 294 894 discloses the similar use of amine-anionic ion pair/wax composites having a  
20 particle size of 1 to 1000 nanometer in liquid compositions.

In preparing lamellar liquid detergent compositions comprising one or more softening-in-the-wash additives,  
25 often instability and/or viscosity problems are observed. The present invention seeks to improve the stability and/or viscosity of these products by using a deflocculating polymer as additive.

30 Preferred fabric softening ingredients for incorporation in lamellar structured compositions of the invention are selected from the groups of

- (i) fabric softening clays;
- 35 (ii) fabric softening cellulose ether materials;

(iii) particles comprising a quaternary ammonium fabric softener, an amine softener material, an amphoteric fabric softener material or mixtures thereof;

5

(iv) mixtures thereof.

Suitable fabric softening clays include low, medium or high swelling clays. Examples of suitable clay materials are Hectorites/ Na Bentonites, for example BENTONE EW and CLARSOL W100; Ca Bentonites, for example CLARSOL KCl, MDO 77/84, LAUNDROSIL DG, LAPORTE CP 103 and MARMORA, or their sodium carbonate activated forms; commercially sodium carbonate activated Ca Bentonite, for example CLARSOL KC2, MDO 81/84, LAUNDROSIL DG AC and DOKUM KARAKAYA; acid activated Ca Bentonites, for example BENTONITE DC and white bentonites, for example STREETLEY NO's 1 and 2. Other suitable clay materials are disclosed in the above mentioned British patent 1,400,898.

Other suitable fabric softening clays are VOLCLAY SPV (origin USA), SURREY NO. 1 (origin USA), EARTH (origin UK), ENVIRONETICS (origin Argentina), CULVIN (origin South Africa), SAN FRAN (origin Argentina), BERKBOND 1 (origin UK), STREETLEY WYOMING (origin USA), MDO 77/84 and ECC (ASB) (both origin Morocco), UBM (origin Brazil), CSM (high CEC Prassa) (origin Greece), GELLWHITE (origin TEXAS USA) and WILLEMSE (origin South Africa).

Preferred clay materials for use in compositions of the invention are montmorillonite clays, more preferably bentonite clays, especially preferred white bentonite clays.

35

The amount of fabric softening clays in compositions of the invention is preferably from 1-25 %, more preferred

from 2-15 %, most preferred from 3-10 % by weight of the composition.

- Preferred fabric softening cellulose ether materials
- 5 are nonionic substituted cellulose ethers having an HLB of between 3.1 and 4.3, a gel point of less than 58°C, said cellulose ether material being substituted with C<sub>1-3</sub> alkyl and/or hydroxyalkyl groups.
- 10 Preferably the substituent groups are selected from the C<sub>2</sub>-C<sub>3</sub> alkyl and C<sub>2</sub>-C<sub>3</sub> mono- or polyhydric hydroxy alkyl groups, or combinations thereof. Especially the use of alkyl hydroxyalkyl cellulose ethers is preferred. Most preferred is the use of ethyl hydroxyethyl substituted
- 15 cellulose ethers. The choice and percentage of substituent groups has a direct influence on the HLB value of the cellulose ether. A suitable method for determining the HLB value of cellulose ethers is the method as described for emulsifiers by J T Davies, 2nd
- 20 Int Congress of Surface Activity 1957, I pp 426-439. This method has been adopted to derive a relative HLB ranking for cellulose ethers by summation of Davies's HLB assignments for substituent groups at the three available hydroxyl sites on the anhydroglucose ring of
- 25 the polymer. The HLB assignments for the substituents groups include the following:

	Residual Hydroxyl	1.9
	Methyl	0.825
30	Ethyl	0.350
	Hydroxy ethyl	1.63
	Hydroxy propyl	1.15
	Hydroxy butyl	0.67.

- 35 The cellulose ethers useful herein are polymers. The gel point of polymers can be measured in a number of ways. In the present context the gel point is measured on a polymer solution prepared at 10 g/l concentration in

deionised water by heating 50 ml solution placed in a beaker, with stirring, at a heating rate of approximately 5°C/minute. The temperature at which the solution clouds is the gel point of the cellulose ether being tested and is measured using a Sybron/Brinkmann calorimeter at 80% transmission/450 nm.

Provided that the HLB and gel point of the polymer fall within the required ranges, the degree of substitution (DS) of the anhydroglucose ring may be any value up to the theoretical maximum value of 3, but is preferably from about 1.7-2.9, there being a maximum of 3 hydroxyl groups on each anhydroglucose unit in cellulose. The expression 'molar substitution' (MS) is sometimes also used in connection with these polymers and refers the number of hydroxyalkyl substituents per anhydroglucose ring and may be more than 3 when the substituents themselves carry further substituents.

The most highly preferred polymers have an average number of anhydroglucose units in the cellulose polymer, or weight average degree of polymerisation, from about 50 to about 1,200. For liquids, it may be desirable to include polymers of relatively low degree of polymerisation to obtain a satisfactory product viscosity.

A number of cellulose ethers suitable for use in the present invention are commercially available, as follows:



	Trade Name	Gel point	°C HLB (Davies)	DS/MS alkyl/ hydroxalkyl
5	BERMOCOLL CST035 (ex Berol Nobel)	35	3.40	)1.4 ethyl )0.5 hydroxyethyl
10	DVT 88 004 (ex Berol Nobel)	37	3.11	)1.5 ethyl )1.0 hydroxyethyl
	TYLOSE MHB 1000 (ex Hoechst)	54	3.52	)2.0 methyl )0.1 hydroxyethyl

15

The amount of cellulose ether be employed in compositions according to the invention is preferably from 0.05 to 5%, more preferably from 0.5 to 3% by weight of the composition.

20

Preferred cellulose ethers for use in compositions of the present invention have an HLB of between 3.3 and 3.8 and a gel point of between 30 and 55°C. Especially preferred is the use of Bermocoll CST035.

25

Preferred particles comprising a quaternary ammonium fabric softener and/or an amine softener material and/or an amphoteric fabric softener material are discrete composites of one or more conventional softening ingredients. Also lamellar droplets of fabric softening materials are considered as particles in accordance with the present invention; preferably however solid particles are used.

35

Suitable quaternary ammonium softeners, amines and amphoteric fabric softening ingredients are for example disclosed in EP 322 270.

Preferably these particles have a weight average particle size of 5 nanometer to 1000 micrometer, more preferred from 10 nanometer to 10 micrometer, most preferred from 50 nanometer to 5 micrometer.

5

Preferably the amount of fabric softening particles is from 1 to 25 % by weight of the composition, more preferred from 2 to 15 %, most preferred from 3 to 10 %.

10

The liquid detergent product

Preferably compositions of the invention are stable. In the context of the present invention, stability for these systems can be defined in terms of the maximum separation compatible with most manufacturing and retail requirements. That is, the 'stable' compositions will yield no more 10 %, preferably no more than 5 %, most preferred no more than 2% by volume phase separation as evidenced by appearance of 2 or more separate phases when stored at 25°C for 21 days from the time of preparation. Especially preferred are compositions which do not yield any phase separation upon storage for 21 days at 25 °C

25

Preferably, compositions of the invention have a pH of between 6 and 14, more preferred from 6.5 to 13, especially preferred from 7 to 12.

30

Compositions of the invention preferably have a viscosity of less than 5,000 mPas at 21 s<sup>-1</sup>, more preferred less than 4000 mPas, most preferred less than 3000 mPas, especially preferred between 100 and 1,000 mPas at 21 s<sup>-1</sup>.

35

Compositions of the invention also comprise detergent active materials, preferably at a level of from 1 to 70% by weight of the composition, more preferred a level of

5 to 40 % by weight, most preferred from 10 to 35 % by weight.

5 In the case of blends of surfactants, the precise proportions of each component which will result in lamellar structures will depend on the type(s) and amount(s) of the electrolytes, as is the case with conventional structured liquids.

10 In the widest definition the detergent-active material in general, may comprise one or more surfactants, and may be selected from anionic, cationic, nonionic, zwitterionic and amphoteric species, and (provided  
15 mutually compatible) mixtures thereof. For example, they may be chosen from any of the classes, sub-classes and specific materials described in 'Surface Active Agents' Vol.I, by Schwartz & Perry, Interscience 1949 and 'Surface Active Agents' Vol.II by Schwartz, Perry & Berch (Interscience 1958), in the current edition of  
20 "McCutcheon's Emulsifiers & Detergents" published by the McCutcheon division of Manufacturing Confectioners Company or in 'Tensid-Taschenbuch', H.Stache, 2nd Edn., Carl Hanser Verlag, München & Wien, 1981.

25 Suitable nonionic surfactants include, in particular, the reaction products of compounds having a hydrophobic group and a reactive hydrogen atom, for example aliphatic alcohols, acids, amides or alkyl phenols with  
30 alkylene oxides, especially ethylene oxide, either alone or with propylene oxide. Specific nonionic detergent compounds are alkyl (C<sub>6</sub>-C<sub>18</sub>) primary or secondary linear or branched alcohols with ethylene oxide, and products made by condensation of ethylene oxide with the reaction products of propylene oxide and ethylenediamine. Other  
35 so-called nonionic detergent compounds include long chain tertiary amine oxides, long-chain tertiary phosphine oxides and dialkyl sulphoxides.

Preferably the level of nonionic surfactants is more than 1 % by weight of the composition, preferably from 2.0 to 20.0% by weight of the composition.

5 Compositions of the present invention may contain synthetic anionic surfactant ingredients, which are preferably present in combination with the above mentioned nonionic materials. Suitable anionic surfactants are usually water-soluble alkali metal salts  
10 of organic sulphates and sulphonates having alkyl radicals containing from about 8 to about 22 carbon atoms, the term alkyl being used to include the alkyl portion of higher acyl radicals. Examples of suitable synthetic anionic detergent compounds are sodium and  
15 potassium alkyl sulphates, especially those obtained by sulphating higher (C<sub>8</sub>-C<sub>18</sub>) alcohols produced, for example, from tallow or coconut oil, sodium and potassium alkyl (C<sub>9</sub>-C<sub>20</sub>) benzene sulphonates, particularly sodium linear secondary alkyl (C<sub>10</sub>-C<sub>15</sub>)  
20 benzene sulphonates; sodium alkyl glyceryl ether sulphates, especially those ethers of the higher alcohols derived from tallow or coconut oil and synthetic alcohols derived from petroleum; sodium coconut oil fatty monoglyceride sulphates and  
25 sulphonates; sodium and potassium salts of sulphuric acid esters of higher (C<sub>8</sub>-C<sub>18</sub>) fatty alcohol-alkylene oxide, particularly ethylene oxide, reaction products; the reaction products of fatty acids such as coconut fatty acids esterified with isethionic acid and  
30 neutralized with sodium hydroxide; sodium and potassium salts of fatty acid amides of methyl taurine; alkane monosulphonates such as those derived by reacting alpha-olefins (C<sub>8</sub>-C<sub>20</sub>) with sodium bisulphite and those derived from reacting paraffins with SO<sub>2</sub> and Cl<sub>2</sub> and  
35 then hydrolyzing with a base to produce a random sulphonate; and olefin sulphonates, which term is used to describe the material made by reacting olefins, particularly C<sub>10</sub>-C<sub>20</sub> alpha-olefins, with SO<sub>3</sub> and then

neutralizing and hydrolyzing the reaction product. The preferred anionic detergent compounds are sodium (C<sub>11</sub>-C<sub>15</sub>) alkyl benzene sulphonates and sodium (C<sub>16</sub>-C<sub>18</sub>) alkyl sulphates.

5

Generally the level of the above mentioned non-soap anionic surfactant materials is from 1-15 % by weight of the composition.

10

Preferably the weight ratio of the above mentioned synthetic anionic surfactants to the above mentioned nonionic surfactant materials is from 10 : 1 to 1 : 10, more preferred from 2 : 1 to 1 : 5, most preferred from 1 : 2 to 1 : 4.

15

It is also possible, and sometimes preferred, to include an alkali metal soap of a mono- or di-carboxylic acid, especially a soap of an acid having from 12 to 18 carbon atoms, for example oleic acid, ricinoleic acid, and fatty acids derived from castor oil, rapeseed oil, groundnut oil, coconut oil, palmkernel oil, alk(en)yl succinates e.g. dodecyl succinate or mixtures thereof. The sodium or potassium soaps of these acids can be used. Preferably the level of soap in compositions of the invention is from 1-40 % by weight of the composition, more preferred from 5-25 %.

20

25

30

Also possible is the use of salting out resistant active materials such as for example described in EP 328 177, especially the use of alkyl poly glycoside surfactants such as for example disclosed in EP 70 074. Also alkyl mono glucosides may be used.

35

The compositions optionally also contain electrolyte in an amount sufficient to bring about lamellar structuring of the detergent-active material. Preferably the compositions contain from 1% to 60%, especially from 10 to 45% of a salting-out electrolyte. Salting-out

electrolyte has the meaning ascribed to in specification EP-A-79 646. Optionally, some salting-in electrolyte (as defined in the latter specification) may also be included.

5

In any event, it is preferred that compositions according to the present invention include detergency builder material, some or all of which may be electrolyte. In this context it should be noted that some detergent active materials such as for example soaps, also have builder properties.

10  
15

Examples of phosphorous-containing inorganic detergency builders include the water-soluble salts, especially alkali metalpyrophosphates, orthophosphates, polyphosphates and phosphonates. Specific examples of inorganic phosphate builders include sodium and potassium tripolyphosphates, phosphates and hexametaphosphates. Phosphonate sequestrant builders may also be used. Sometimes it is however preferred to minimise the amount of phosphate builders.

20  
25

Examples of non-phosphorus-containing inorganic detergency builders, when present, include water-soluble alkali metal carbonates, bicarbonates, silicates and crystalline and amorphous aluminosilicates. Specific examples include sodium carbonate (with or without calcite seeds), potassium carbonate, sodium and potassium bicarbonates, silicates and zeolites.

30

In the context of inorganic builders, we prefer to include electrolytes which promote the solubility of other electrolytes, for example use of potassium salts to promote the solubility of sodium salts. Thereby, the amount of dissolved electrolyte can be increased considerably (crystal dissolution) as described in UK patent specification GB 1 302 543.

35

Examples of organic detergency builders, when present, include the alkaline metal, ammonium and substituted ammonium polyacetates, carboxylates, polycarboxylates, polyacetyl carboxylates and polyhydroxysulphonates.

5 Specific examples include sodium, potassium, lithium, ammonium and substituted ammonium salts of ethylenediaminetetraacetic acid, nitrilotriacetic acid, oxydisuccinic acid, melitic acid, benzene polycarboxylic acids, CMOS, tartrate mono succinate, tartrate di succinate and citric acid. Citric acids or salts thereof are preferred builder materials for use in compositions of the invention.

10

In the context of organic builders, it is also desirable to incorporate polymers which are only partly dissolved, in the aqueous continuous phase as described in EP 301.882. This allows a viscosity reduction (due to the polymer which is dissolved) whilst incorporating a sufficiently high amount to achieve a secondary benefit, especially building, because the part which is not dissolved does not bring about the instability that would occur if substantially all were dissolved. Typical amounts are from 0.5 to 4.5% by weight.

15

20

It is further possible to include in the compositions of the present invention, alternatively, or in addition to the partly dissolved polymer, yet another polymer which is substantially totally soluble in the aqueous phase and has an electrolyte resistance of more than 5 grams sodium nitrilotriacetate in 100ml of a 5% by weight aqueous solution of the polymer, said second polymer also having a vapour pressure in 20% aqueous solution, equal to or less than the vapour pressure of a reference 2% by weight or greater aqueous solution of polyethylene glycol having an average molecular weight of 6000; said second polymer having a molecular weight of at least 1000. Use of such polymers is generally described in our

25

30

35

EP 301,883. Typical levels are from 0.5 to 4.5% by weight.

Preferably the level of non-soap builder material is  
5 from 5-40 % by weight of the composition, more preferred  
from 5 to 25 % by weight of the composition.

Apart from the ingredients already mentioned, a number  
of optional ingredients may also be present, for  
10 example lather boosters such as alkanolamides,  
particularly the monoethanolamides derived from palm  
kernel fatty acids and coconut fatty acids, lather  
depressants, oxygen-releasing bleaching agents such as  
sodium perborate and sodium percarbonate, peracid bleach  
15 precursors, chlorine-releasing bleaching agents such as  
trichloroisocyanuric acid, inorganic salts such as  
sodium sulphate, and, usually present in very minor  
amounts, fluorescent agents, perfumes, enzymes such as  
proteases, amylases and lipases (including Lipolase  
20 (Trade Mark) ex Novo), anti-redeposition agents,  
germicides and colourants.

Compositions of the invention may be prepared by any  
conventional method for the preparation of liquid  
25 detergent compositions. A preferred method involves the  
dispersing of the electrolyte ingredient together with  
the minor ingredients except for the temperature  
sensitive ingredients -if any- in water of elevated  
temperature, followed by the addition of the builder  
30 material- if any-, the detergent active material  
(optionally as a premix) under stirring and thereafter  
adding the softener materials, cooling the mixture and  
adding any temperature sensitive minor ingredients such  
as enzymes perfumes etc. The deflocculating polymer may  
35 advantageously be added after the electrolyte  
ingredients, the builder ingredients or just before  
cooling. If a cellulose ether material is used,  
preferably this is added as the final ingredient.



In use the detergent compositions of the invention will be diluted with wash water to form a wash liquor for instance for use in a washing machine. The concentration of liquid detergent composition in the wash liquor is preferably from 0.1 to 10 %, more preferred from 0.1 to 3% by weight.

The invention will now be illustrated by way of the following Examples.

EXAMPLE I

The following liquid lamellar structured detergent compositions were prepared:

5	INGREDIENT (wt %)	A	B	C	D	E
	-----					
	Na-Oleate	26	26	26	26	26
	Na-Las	8	8	8	8	8
10	Synperonic A7	5	5	5	5	5
	Na-citrate	20	20	20	20	20
	Polymer <sup>1)</sup>	1	1	1	1	-
	Bermocoll CST 035	0	0.5	0.5	0.5	-
	water			balance		

15

<sup>1)</sup> Deflocculating polymer of formula I, wherein q, p and r are 0, v=1, x=25, y=0, R<sup>1</sup> is - CO - O -, R<sup>2</sup> is absent R<sup>3</sup> is absent, R<sup>4</sup> is - C<sub>12</sub>H<sub>25</sub>, R<sup>5</sup> is -H, R<sup>6</sup> is - CH<sub>3</sub> and A<sup>1</sup> is Na. The molecular weight of the polymer is about 3.5 K.

20

Composition A was prepared by adding the ingredients to water of 50°C under stirring, in the following order: Na-citrate, NaOH (for neutralising the active ingredients), polymer, Oleic acid, premix of Las acid and Synperonic A7. Composition B was made by the same method, whereby the Bermocoll CST 035 was added as the last ingredient. Composition C was made by the same method as composition A, whereby the Bermocoll CST 035 was added as the first ingredient. Composition D was prepared by adding the ingredients to water of 50°C under stirring, in the following order: Na-citrate, NaOH, Oleic acid, premix of Na-Las (acid form) and Synperonic A7, Bermocoll CST 035 and deflocculating polymer. Composition E was prepared by mixing the ingredients in the order as listed for composition D.

Composition A was unstable (more than 10 % phase separation within 3 weeks) and had a viscosity of about 180 mPas at 21 s<sup>-1</sup>. Composition B was more stable than composition A, but still showed some phase separation, the viscosity of the product was about 145 mPas at 21 s<sup>-1</sup>. Composition C was stable (no phase separation observed after storage for 3 weeks) and had a viscosity of about 1150 mPas at 21 s<sup>-1</sup>. Composition D was stable (no phase separation observed after storage from 3 weeks) and had a viscosity of about 300 mPas at 21 s<sup>-1</sup>. Composition E was unstable (more than 10 % phase separation within three weeks) and had a viscosity of about 2,000 mPas at 21 s<sup>-1</sup>.

This example illustrates that compositions which are in itself unstable (composition E), can be made more stable and/or less viscous by incorporating therein the combination of cellulose ether materials and deflocculating polymers. Also a stability increase and/or viscosity decrease may be observed in comparing a composition containing a deflocculating polymer to a composition comprising a deflocculating polymer in combination with a cellulose ether materials. Similar results were obtained when comparing a formulation comprising the cellulose ether component in the absence of deflocculating polymer to compositions B and C.

All compositions comprising deflocculating polymers in combination with Bermocoll CST 035 were capable of providing softness to fabrics.

EXAMPLE II

The following compositions were made:

5	Ingredient (wt %)	A	B	C	D	E	F	G	H
	-----								
	NaLAS	28	28	28	28	28	28	28	28
	Synperonic A7	12	12	12	12	12	12	12	12
	polymer <sup>1)</sup>	--	1	--	1	--	1	--	1
10	Na-citrate	20	20	20	20	20	20	20	20
	Bentone 34 <sup>2)</sup>	--	--	5	5	--	--	2	2
	Clarsol KCl <sup>3)</sup>	--	--	--	--	5	5	--	--
	Water				balance				

15

1) Deflocculating polymer of formula I, wherein q, p and r are 0, v=1, x=25, y=0, R<sup>1</sup> is - CO - O -, R<sup>2</sup> is absent R<sup>3</sup> is absent, R<sup>4</sup> is - C<sub>12</sub>H<sub>25</sub>, R<sup>5</sup> is -H, R<sup>6</sup> is - CH<sub>3</sub> and A<sup>1</sup> is Na. The molecular weight of the polymer is about 3.5 K.

20

2) Hydrophobically modified clay (ex NL Industries)

3) Bentonite clay (ex CECA)

25

The order of addition to water of 50°C was Na-citrate, NaOH (for neutralising the active ingredients), Oleic acid, premix of Las acid and Synperonic A7, clay (if present) and deflocculating polymer.

30

Composition A was unstable and had a viscosity of about 2,000 mPas at 21 s<sup>-1</sup>. Composition B was stable and had a viscosity of about 100 mPas at 21 s<sup>-1</sup>. These examples confirm (see EP 89201530.6) that deflocculating polymers can be used for increasing the stability and/or decreasing the viscosity of lamellar structured liquid detergent compositions.

35

Composition C was unstable and had an unacceptable high viscosity of about 5,700 mPas at 21 s<sup>-1</sup>. Composition D

was stable and had an acceptable, although relatively high, viscosity. Composition E was unstable and had a viscosity of about 2400 mPas at 21 s<sup>-1</sup>. Composition F was stable and had a viscosity of about 380 mPas at 21 s<sup>-1</sup>.

Composition G was unstable and had a viscosity of about 3,500 mPas at 21 s<sup>-1</sup>. Composition H was stable and has a viscosity of about 290 mPas at 21 s<sup>-1</sup>.

These examples clearly illustrate that the stability increase and/or the viscosity decrease obtained by incorporating deflocculating polymers can be maintained, even in the presence of softening clay materials, which were hitherto believed to be unsuitable for incorporation in liquid detergent compositions.

All compositions containing clay softener materials were capable of providing increased softness to fabrics in the wash.

material specification

Na-LAS	Sodium linear C <sub>12</sub> alkyl benzene sulphonate
25 Synperonic A7	C <sub>12-15</sub> alcohol, ethoxylated with 7 EO groups, ex ICI.

CLAIMS

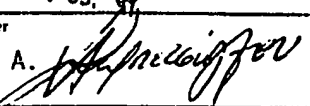
1. A liquid detergent composition comprising a dispersion of lamellar droplets of detergent active materials in an aqueous continuous phase and one or more ingredients for providing softness to fabrics, said composition also comprising a deflocculating polymer.
2. A composition according to claim 1, wherein the deflocculating polymer is selected from the group of polymers of formula I, II or III, as defined hereabove.
3. A composition according to claim 1, wherein the corresponding composition minus the deflocculating polymer is less stable and/or has a higher viscosity.
4. A composition according to claim 1, wherein the fabric softening material is selected from the following groups:
  - (i) fabric softening clays;
  - (ii) fabric softening cellulose ether materials;
  - (iii) particles comprising a quaternary ammonium fabric softener, an amine softener material, an amphoteric fabric softener material or mixtures thereof;
  - (iv) mixtures thereof.
5. A composition according to claim 4, wherein the fabric softening clay is a montmorillonite clay material.

6. Method of preparing a composition in accordance with claim 4, wherein the fabric softening material is a fabric softening cellulose ether material and wherein this ingredient is added to the composition as the final ingredient.

## INTERNATIONAL SEARCH REPORT

International Application No.

PCT/EP 90/01815

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) <sup>6</sup>		
According to International Patent Classification (IPC) or to both National Classification and IPC Int.Cl. 5 C11D17/00 ; C11D3/37		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>7</sup>		
Classification System	Classification Symbols	
Int.Cl. 5	C11D	
Documentation Searched other than Minimum Documentation to the extent that such Documents are included in the Fields Searched <sup>8</sup>		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup></b>		
Category <sup>10</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
A	EP,A,0301884 (UNILEVER) 01 February 1989 see page 4, lines 5 - 59 see page 5, lines 55 - 64; claims 19-21 ---	1, 3, 4
A	EP,A,0303473 (ALBRIGHT & WILSON LTD) 15 February 1989 see page 3, lines 19 - 41; claims 1, 2 ---	1, 4
A	EP,A,0291261 (UNILEVER) 17 November 1988 see page 3, lines 4 - 49; claims 1, 4 (cited in the application) ---	1, 4, 5
A	EP,A,0213730 (UNILEVER) 11 March 1987 see column 2, line 1 - column 8, line 49 see column 12, lines 22 - 23; claims 1-6 (cited in the application) --- -/-	1, 4
<p><sup>10</sup> Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"I" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"R" document member of the same patent family</p>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
07 FEBRUARY 1991	07.03.91	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	SERBETSOGLU A. 	



III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
X, P	EP, A, 0346995 (UNILEVER) 20 December 1989 see page 15, lines 55 - 57; claims 1-5, 24, 33; table 1t (cited in the application) ---	1-4

**ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO.**

*PCT/EP 90/01815*  
SA 41089

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.  
The members are as contained in the European Patent Office EDP file on  
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

07/02/91

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A-0301884	01-02-89	None		
EP-A-0303473	15-02-89	AU-A-	2062188	16-02-89
		GB-A-	2208520	05-04-89
		JP-A-	1068573	14-03-89
EP-A-0291261	17-11-88	AU-A-	1581288	17-11-88
		JP-A-	1011199	13-01-89
EP-A-0213730	11-03-87	AU-B-	569662	11-02-88
		AU-A-	6057786	05-02-87
		DE-A-	3661139	15-12-88
		JP-A-	63035699	16-02-88
EP-A-0346995	20-12-89	AU-A-	3626789	14-12-89
		AU-A-	3626989	14-12-89
		AU-A-	3632989	14-12-89
		EP-A-	0346993	20-12-89
		EP-A-	0346994	20-12-89
		JP-A-	2034699	05-02-90
		JP-A-	2034700	05-02-90
		JP-A-	2038500	07-02-90